The University of Chicago

THE EFFECT OF ALKALI UPON PORTLAND CEMENT

A DISSERTATION

SUBMITTED TO THE FACULTY
OF THE OGDEN GRADUATE SCHOOL OF SCIENCE
IN CANDIDACY FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

BY

KARL THEODOR STEIK

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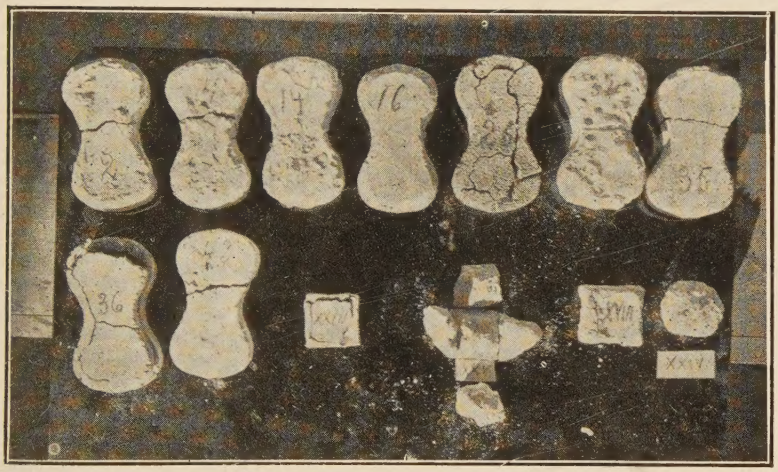

Cement in different stages of disintegration.

THE EFFECT OF ALKALI UPON PORTLAND CEMENT—II

Bulletins will be sent free upon request.
Address: Director of Experiment Station, Laramie, Wyoming.

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The Effect of Alkali Upon Portland Cement—II

KARL STEIK

INTRODUCTION.*

Of the salts which constitute the so-called "alkali", the following were used in the determination of their effect on Portland cement: The sulfates of sodium and magnesium, chlorides of sodium and magnesium and the carbonate of sodium. The nitrates occur only in very small quantities and therefore are not detrimental to any extent in regard to the cement problems. Cases are mentioned in the literature where concrete is supposed to have been damaged by water which had percolated through gypsum beds, therefore, effects of solution of calcium sulphate, too, were investigated.

In the Western States the number of different salts present in the so-called "alkali" varies according to local conditions. The two most abundant and frequent salts are the sulfates of sodium and magnesium. The carbonate of sodium is present in the black alkali. The concentration of the salts in waters varies according to the localities and seasons of the year. Some of the alkali lakes are filled with saturated solutions during dry seasons and in many of them solid deposits occur on the lake bottoms.

Experiments were conducted with solutions of only one salt at different concentrations in order to determine the effect of each salt separately. Solutions were also used which contained two, three and four different salts at different concentrations. In order to determine the relative merits in regard to resisting the action of alkali, neat cement and mortars of different concentration were used. For comparison, several brands of cement were tried, but most of the experiments were carried out on "Ideal" cement. In all cases the amount of solution per gram of cement or mortar was the same.

Experience showed that the reaction of alkali on neat Portland cement was very slow; consequently, for the purpose of ob-

*A progress report on this problem was made in Bulletin 113 of the Wyoming Station. Much of the work outlined on the following pages appeared in the earlier publication but is included at this time to round out and complete the final report.

taining more marked results, some experiments were conducted with solutions kept at temperature of boiling water during eight hours a day for eighteen months. In connection with these experiments, the effect of periodical wetting and drying was tested and also the effect of treating the cement with large quantities of hot distilled water.

CHEMICAL CHANGES

The chemical reactions which take place between the constituents of the alkali were judged from the reaction products. In solutions of sodium sulfate, or magnesium sulfate singly or combined, deposits of crystalline calcium sulfate were obtained as shown in Figures 1 and 2. In dilute solutions, single crystals were more likely to form, as in Figure 1; in more concentrated solutions crystalline rosette-like aggregates were formed, as in Figure 2.

Fig. 1.

On cement kept in water, crystalline and amorphous deposits of $Ca(OH)_2$—calcium hydroxide—were obtained, as shown in Figures 3 and 4. The surfaces of cement kept in a solution of sodium carbonate were either entirely or partially covered with amorphous calcium carbonate, $CaCO_3$, as shown in Figure 5.

The magnesium hydroxide which was formed in solutions of magnesium sulfate was amorphous, and, usually, mixed with amorphous calcium sulfate. Deposits of crystalline magnesium hydroxide were obtained on surfaces of cement kept in hot solutions of magnesium chloride. The crystals formed small nodules, as shown in Figure 6.

Fig. 2.

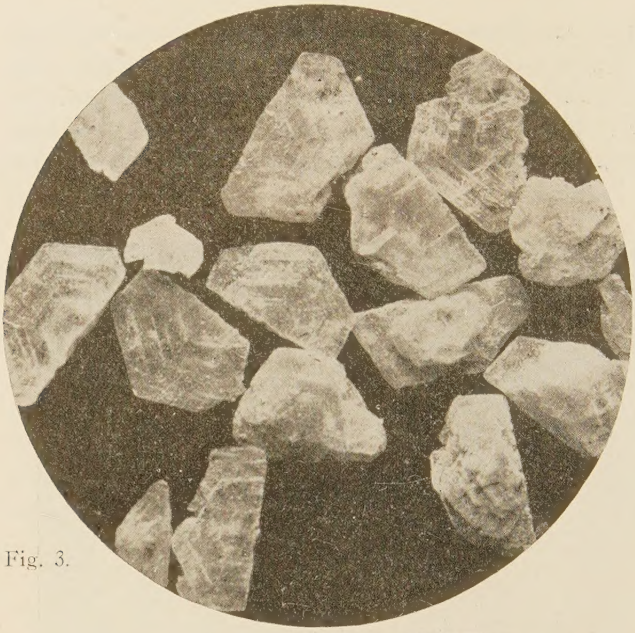

Fig. 3.

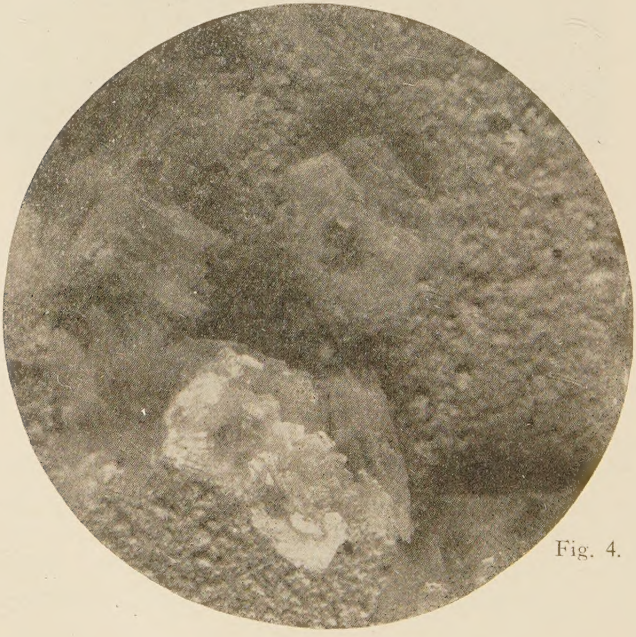

Fig. 4.

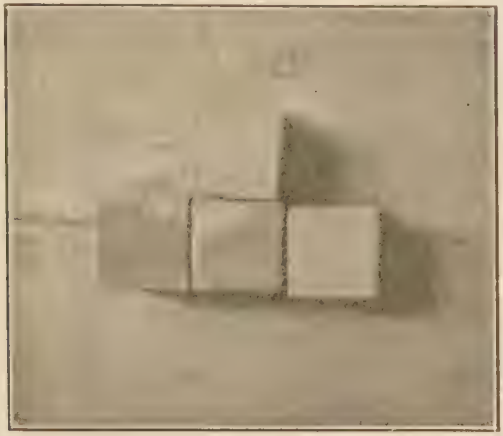

Fig. 5

Fig. 6

Besides these products of reaction, one more was obtained from cement which was kept in a 5 per cent solution of sodium chloride. This solution was not changed during the entire time of experiments and the crystals appeared after a period of about 3 years. In other cases, fresh solutions were used after each testing of the compression and tension strength of the cement. The crystals, after cleaning off the adhering matter from their surfaces, gave the following analytical results: SiO_2, 40.14 per

cent; Al_2O_3, 31.48 per cent; Fe_2O_3, 0.11 per cent; CaO, 10.09 per cent; Na_2O, 14.13 per cent; Cl, 4.32 per cent. Figure 7 shows these crystals.

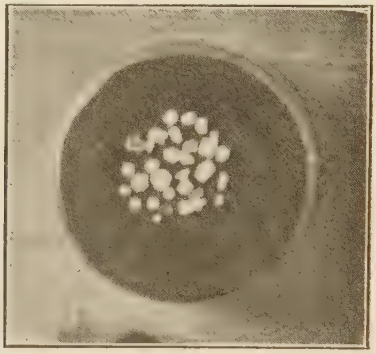

Fig. 7.

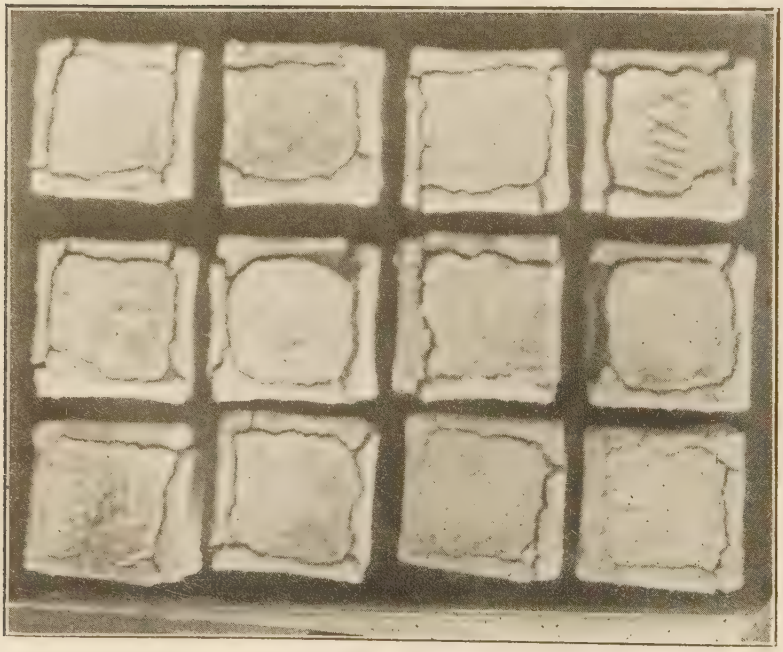

Fig. 8.

From the above results, it appears that the following reactions took place in different solutions used:

$Ca(OH)_2 + Na_2SO_4 + aq. \rightarrow CaSO_4.2H_2O + 2NaOH + aq.$;
$Ca(OH)_2 + MgSO_4 + aq. \rightarrow CaSO_4.2H_2O + Mg(OH)_2 + aq.$;
$Ca(OH)_2 + Na_2CO_3 + aq. \rightarrow CaCO_3 + 2NaOH + aq.$

The analysis of the calcium sulfate crystals gave the following, showing it to be $CaSO_4.2H_2O$: Water, 21.0%; CaO, 32.5%; SO_3, 46.3%.

PHYSICAL CHANGES.

The reaction of sodium and magnesium sulfates produced characteristic changes, which were especially apparent in the case of mortars. From the appearance of the mortar, it was possible

Fig. 9.

to tell which of the salts had been acting. Figure 8 shows the cracks formed on a 1:4 mortar which was immersed in a solution of sodium sulfate. Notice that every cube in the set has been affected in the same manner. In figure 9 is demonstrated the effect of a magnesium sulfate solution on 1:4 mortar. The solution of sodium sulfate and the solution of magnesium sulfate were of the same normality. Figure 10 also shows the effect of magnesium sulfate, but at a somewhat earlier stage than in figure 9. The little clumps of needles are crystals of calcium sulfate.

As the concentration of cement in the mortar increases, the cracks appear nearer the edges of the briquets and cubes and thin layers gradually fall off, as shown in figure 11. In figure 12, from left to right is shown a cube as it looks when the first layer is nearly off, the thickness of the layer and the cube with first layer removed.

Cement which was immersed in 0. 5 N. sulfuric acid showed

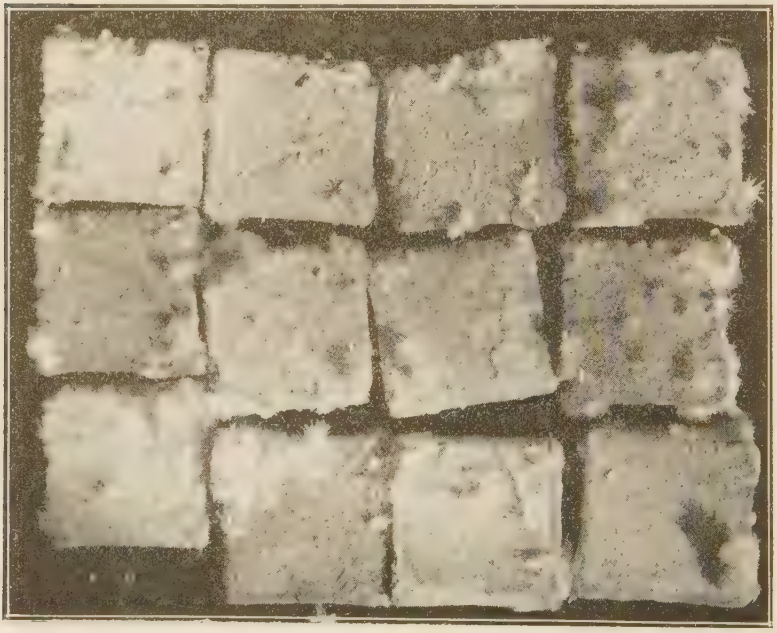

Fig. 10.

the same kind of results as cement in a solution of sodium sulfate. In this experiment the acid was renewed when it became neutralized. The effects of hydrochloric acid of the equivalent con-

Fig. 11.

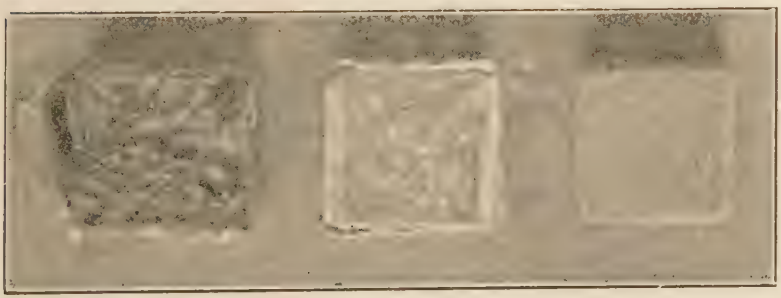

Fig. 12.

centration of the sulfuric acid used were somewhat different. Instead of parallel cracks produced along the edges of cubes, as in case of sulphuric acid, minute cracks in large numbers were produced all over the surfaces. Figures 13 and 14 represent the results of the action of sulfuric and hydrochloric acid respectively.

Fig. 13

Fig. 14.

Figure 15 shows the results produced by the following treatment: The cubes were covered with distilled water and warmed on a water-bath. The water was allowed to evaporate and the cement dried. Then it was covered with water again and the process repeated. After a sufficient length of time cracks were formed which extended from edge to edge. No cracks were formed on cubes which were treated in the same way, except that they were always covered with water. Consequently the cracking was due to alternate wetting and drying of the cement.

In order to test the alkali resisting quality of mortars with varying proportions of sand, mortars were made up containing as many as 10 parts of sand to one part of cement. Figure 16 shows a comparison between neat cement and mortars of different dilutions which were placed in a normal solution of sodium chloride and sodium sulfate.

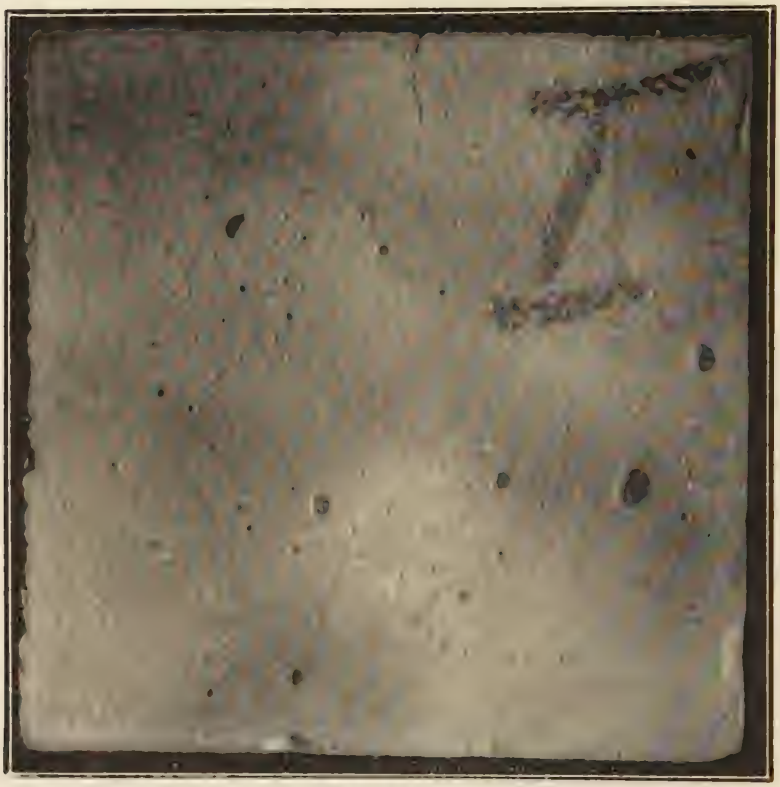

Fig. 15.

Fig. 16.

Top row left to right: Neat cement in distilled water; neat cement which was heated on water bath and was periodically either covered with water, or dry; the next ones are in order: neat cement; 1:1; 1:2; 1:3; 1:4; 1:5; 1:6, and 1:7 mortars, all in a normal solution of normal sodium chloride and sodium sulfate for a period of 6 months. Notice the characteristic cracking produced by sodium sulfate. All specimens, except the first and third show the effects of treatment. The neat cement in the solution looks as well as the neat cement in distilled water.

Fig. 17.

Figure 17 represents the effects produced in a normal solution of magnesium chloride and magnesium sulfate. Except for the first cube on the left in the top row, which is neat cement in distilled water, the following cubes from left to right had compositions: neat cement; 1:1; 1:2; 1:3; 1:4; 1:5; 1:6; 1:7. During the entire period of 6 months the specimens were not disturbed, but even then the 1:7 mortar had crumbled away. Notice the bulging which is characteristic of the action of magnesium sulfate.

In figure 18 cubes 15, 17 and 19 are 1:1, 1:2 and 1:3 mortars respectively, placed in a normal solution of sodium chloride and sodium sulfate. Numbers 16, 18 and 20 have the same respective

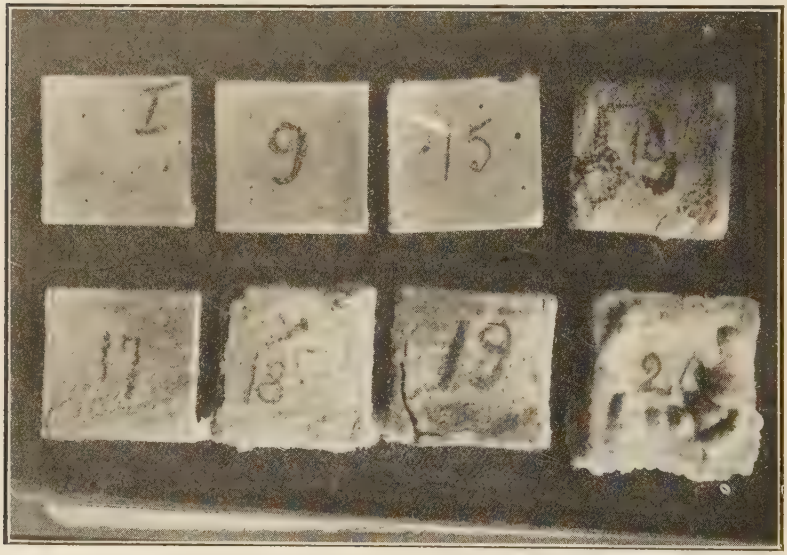

Fig. 18.

composition as the ones above, but these were in a normal solution of magnesium chloride and magnesium sulfate, for a period of 6 months. Notice how the cubes in the solution of magnesium salts have expanded and, judging from appearance, have disintegrated more. Numbers 1 and 9 are neat cement in distilled water. All the above illustrations go to show that as the sand

content of the mortar increases, its resistance against the action of alkali decreases.

Of the different brands of cement only two were claimed to be alkali-resisting, the "Iron ore" cement, and the "Alkali-proof" cement. In regard to the first one, it was impossible to tell from the appearance whether or not it had been affected. The first five briquets and cubes in figure 19 were made of "alkali-proof" cement. It is apparent that a 5 per cent magnesium sulfate solution (first) and a 5 per cent sodium carbonate solution (second) had some deteriorating effects. Briquet marked 59 was coated with Toch's No. 232 R. I. W.; the next to the right was coated with Toch's No. 44 R. I. W. This coating was almost gone after 24 months, after which the above picture was taken.

Fig. 19.

CHANGES IN STRENGTH OF NEAT CEMENT AND MORTARS.

The tables on the following pages set forth clearly some of the results obtained in the cement investigational work. Additional detailed data may be found in Wyoming Bulletin 113.

TABLE I—*Showing the Average Strength of Cement Blocks Before*

Lab No.	SOLUTION	Before immersion	
		Compress	Tension
		lbs.	lbs.
	I. Neat Ideal in various solutions:		
	(1) In distilled water for comparison.		
15	Distilled water	7826	494
	(2) In solutions of single salts.		
	(a) 7 days in water before immersion.		
1	Sol. 1, NaCl, 5 per cent	6745	284
2	Sol. 2, $MgSO_4$, 5 per cent	7939	664
3	Sol. 3, Na_2SO_4, 1 per cent	8827	455
4	Sol. 4, Na_2SO_4, 5 per cent	7708	588
5	Sol. 5, Na_2SO_4, 10 per cent	8031	688
38	NaOH 5 per cent	5802	594
	(b) 14 days in water before immersion.		
6	Sol. 4, Na_2SO_4, 5 per cent	10815	638
7	Sol. 1, NaCl, 5 per cent	8950	525
8	Sol. 6, Na_2CO_3, 5 per cent	9663	662
9	Sol. 7, $NaHCO_3$, 5 per cent	9453	423
12	Sol. 8, NaCl, 7 per cent	11700	437
	(c) 14 days in water and 3 months in air before immersion.		
10	Sol. 8, NaCl, 1 per cent	5791	774
11	Sol. 6, Na_2CO_3, 5 per cent	10467	712
	(3) Neat Ideal in solutions of mixed salts.		
	(a) 7 days in water before immersion.		
17	Sol. 11, $CaCl_2$, MgCl, 1.33 per cent each	5723	400
16	Sol. 10, NaCl, Na_2SO_4, $MgCl_2$, $MgSO_4$, 1.25 per cent each	8552	337
	(b) 3 months in water before immersion.		
14	Sol. 10, (See No. 16)	7090	455
	(c) 48 hours in damp oven before immersion.		
33	Sol. 10, NaCl, Na_2SO_4, $MgCl_2$, $MgSO_4$, 1.25 per cent each	4035	340
	(4) Neat Ideal to show effects of titration.		
37	In water. Titrated with H_2SO_4*	5288	326
43	Sol. 14 NaCl, Na_2SO_4, 2.5 per cent each. Titrated weekly†	7162	261
39	In water. Titrated daily‡	4760	387
45	Sol. 4, Na_2SO_4, 5 per cent. Titrated weekly§	6174	276

and After Being in Salt Solutions for Various Periods.

After being in solution:									
12 months		24 months		30 months		40 months		84 months	
Compress	Tension	Compress	Tension	Compress	Tension	Compress	Tension	Compress	Tension
lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
7145	716	9560	745	10907	677	9877	678	16970	252
9675	994	10185	1017	10452	910	7527	747	13057	197
11615	482	11310	289	10030	651	8073	612	9472	202
10687	400	10712	503	10282	725	9047	698	11742	231
8457	644	7045	716	6482	701	6523	632	8525	297
11577	660	11597	409	11265	280	11460	377	13887	350
8685	905	9965	920	8515	920	7383	768	16107	.....
9342	669	5500	297	4415	655	5050	455	4325	305
8597	905	10295	846	8030	762	.....	.....	.....	.....
10660	830	10327	717	9907	729	10393	685	15375	.....
8942	847	8882	757	9750	729	12270	712	10632	629
9922	779	11390	948	10217	892	9503	793	16017	220
8740	619	9215	749	8505	640	7950	593	11052	231
11540	701	.....	.....	11235	672	10633	550	10732	332
7837	336	8860	844	7960	797	8703	672	10447	282
11167	802	8300	849	8120	745	7850	773	.....	120
10355	916	7680	794	8085	807	7553	860	5252	34
10440	297	9880	1105	7325	1131	7920	1175	10100	211
9622	726	10165	667	10650	679	10640	255	.....	.....
12570	581	11330	876	10827	720	10020	980	13380	371
10240	475	10565	836	12100	821	10607	805	16600	214
10522	902	9885	804	9287	860	9660	740	.....	.....

TABLE II—*Showing Change of Strength of Cement Blocks During a Period Same Cement at the*

Lab No.	SOLUTION	12 months			
		Comp.	Tens'n	Ave.	Comp.
	I. Neat Ideal in various solutions:	%	%	%	%
	(1) In distilled water for comparison.				
15	Distilled water	−8.7	+44.8	+18.0	+35.1
	(2) In solutions of single salts.				
	(a) 7 days in water before immersion.				
1	Sol. 1, NaCl, 5 per cent	+43.4	+250.0	+146.7	+5.2
2	Sol. 2, $MgSO_4$, 5 per cent	+46.3	−27.8	+9.2	−2.6
3	Sol. 3, Na_2SO_4, 1 per cent	+21.0	−12.0	+5.5	+0.2
4	Sol. 4, Na_2SO_4, 5 per cent	+9.7	+9.5	+9.6	−16.6
5	Sol. 5, Na_2SO_4, 10 per cent	+44.1	−4.0	+20.0	+0.2
38	5 per cent NaOH	+49.6	+52.3	+50.9	+14.7
	(b) 14 days in water before immersion.				
6	Sol. 4, Na_2SO_4, 5 per cent	−13.6	+4.8	−4.4	−41.1
7	Sol. 1, NaCl, 5 per cent	−3.9	+72.3	+34.2	+19.7
8	Sol. 6, Na_2CO_3	+10.3	+25.3	+17.8	−3.1
9	Sol. 7, $NaHCO_3$, 5 per cent	−5.4	+100.2	+47.4	−0.6
12	Sol. 8, NaCl, 1 per cent	−15.1	+78.2	+31.5	+14.7
	(c) 14 days in water and 3 months in air before immersion.				
10	Sol. 8, NaCl, 1 per cent	+50.9	−20.0	+15.4	+5.4
11	Sol. 6, Na_2CO_3, 5 per cent	+20.2	−1.5	+9.3	. .
	(3) Neat Ideal in solutions of mixed salts.				
	(a) 7 days in water before immersion.				
17	Sol. 11, $CaCl_2$, $MgCl_2$, NaCl, 1.33 per cent each	+36.9	−16.0	+10.4	+13.0
16	Sol. 10, NaCl, Na_2SO_4, $MgCl_2$, $MgSO_4$, 1.25 per cent each	+30.5	+137.9	+84.2	−25.6
	(b) 3 months in water before immersion.				
14	Sol. 10, NaCl, Na_2SO_4, $MgCl_2$, $MgSO_4$, 1.25 per cent each	+46.5	+101.3	+73.9	−25.7
	(c) 48 hours in damp oven before immersion.				
33	Sol. 10, NaCl, Na_2SO_4, $MgCl_2$, $MgSO_4$, 1.25 per cent each	+158.7	−12.3	+73.2	−5.3
	(4) Neat Ideal to show effects of titration.				
37	In water. Titrated with H_2SO_4*	+81.9	+133.7	+107.8	+5.6
43	Sol. 14, NaCl, Na_2SO_4, 2.5 per cent each. Titrated weekly†	+74.6	+122.3	+98.4	−9.4
39	In water. Titrated daily‡	+115.1	+22.7	+68.9	+3.1
45	Sol. 4, Na_2SO_4, 5 per cent. Titrated weekly§	+70.3	+226.8	+148.5	−6.0

*Titrated daily; water changed weekly.
†Water not changed.
‡Water changed after each test for strength.
§Water changed after each test for strength.

in Salt Solutions Expressed as Per Cent, Computed on the Strength of the Last Preceding Test.

After being in solution:										
24 months		30 months			40 months			84 months		
Tens'n	Ave.	Comp.	Tens'n	Ave.	Comp.	Tens'n	Ave.	Comp.	Tens'n	Ave.
%	%	%	%	%	%	%	%	%	%	%
+4.0	+19.5	+14.1	—9.1	+2.4	—20.2	+0.1	—10.0	+71.6	—62.8	+4.4
+2.3	+3.7	+2.6	—10.5	—3.9	—27.9	—16.8	—22.3	+73.4	—73.6	—0.1
—40.0	—21.3	—11.2	+125.2	+57.0	—19.3	—5.9	—20.9	+17.2	—66.9	—29.8
+101.0	+50.6	—4.0	—10.0	—7.0	—11.9	—3.7	—7.8	+29.7	—66.9	—18.6
+11.1	—2.7	—7.9	—2.0	—4.9	+0.6	—9.8	—4.6	+30.6	—53.0	—11.2
—38.0	—18.9	—2.8	—31.5	—17.1	—7.1	+34.6	+13.7	+21.1	—7.1	+7.0
+1.5	+8.1	—4.5	0	—2.2	—15.3	—16.5	—15.9	—118.1	.....	.....
—55.6	—48.3	—19.7	+123.9	+52.1	+14.3	—30.5	—8.1	—14.3	—33.6	—33.6
—6.5	+6.6	—22.0	—9.9	—15.8	.....	.....	.....	.....	.....	.....
—13.6	—8.3	—4.0	+0.4	—1.8	+4.9	—4.8	0	+47.3	.....	.....
—10.6	—5.6	+9.7	—3.7	+3.0	+25.8	—2.3	+11.7	—13.3	—11.6	—12.4
+21.6	+18.6	—10.2	—5.9	—8.0	—6.9	—11.1	—9.0	+68.5	—72.2	—1.8
+21.0	+13.2	—7.7	—14.5	—11.1	—6.5	—7.3	—6.9	+39.2	—61.0	—0.9
.....	.....	—2.6	—4.1	—3.3	—5.3	—18.1	—11.7	+5.9	—31.6	—18.3
+151.1	+82.0	—10.0	—5.5	—11.8	+8.5	—15.6	—3.5	+20.0	—58.0	—19.0
—5.8	—9.9	—2.1	—12.2	—7.7	—3.3	+3.7	+0.2	.....	—84.4	.....
—13.3	—19.5	+5.2	+1.6	+3.4	—6.5	+6.5	0	—23.4	—18.0	—36.3
+272.0	+133.3	—5.6	+2.3	—1.6	+8.1	+3.9	+6.0	+27.5	—82.0	—27.2
—12.4	—3.9	+4.7	+1.7	+3.2	—0.1	—62.4	—31.2	.....	.....	.....
+50.7	+20.6	—4.4	—17.8	—11.1	—7.4	+22.2	+7.4	+33.5	—62.1	—19.3
+76.0	+34.5	+14.4	—1.7	+6.3	—12.3	—1.9	—7.1	+56.5	—73.4	—8.4
—10.8	—8.4	—6.0	+6.9	+0.4	+4.0	—13.9	—4.9	.....	.....	.....

TABLE III—*Showing the Strength of Cement Blocks Before and After of Cement Blocks in Water*

Lab No.	SOLUTION	Before Immersion			12
		Comp.	Tension	Average	Comp.
		%	%	%	%
	I. Neat Ideal in various solutions:				
	(1) In distilled water for comparison.				
15	Neat Ideal. In distilled water	100	100	100	100
	(2) In solutions of single salts.				
	(a) 7 days in water before immersion.				
1	Sol. 1, NaCl, 5 per cent	86.1	57.4	71.7	135.4
2	Sol. 2, $MgSO_4$, 5 per cent	101.4	134.4	117.9	162.5
3	Sol. 3, Na_2SO_4, 1 per cent	112.7	92.1	102.4	149.5
4	Sol. 4, Na_2SO_4, 5 per cent	98.4	119.0	108.7	118.0
5	Sol. 5, Na_2SO_4, 10 per cent	102.6	139.2	120.9	162.2
38	5 per cent NaOH	74.1	120.2	97.1	121.5
	(b) 14 days in water before immersion.				
6	Sol. 4, Na_2SO_4, 5 per cent	138.1	129.1	133.6	130.7
7	Sol. 1, NaCl, 5 per cent	114.2	106.3	110.2	120.3
8	Sol. 6, Na_2CO_3, 5 per cent	123.5	134.0	128.8	149.2
9	Sol. 7, $NaHCO_3$, 5 per cent	120.8	85.6	108.2	125.4
12	Sol. 8, NaCl, 1 per cent	149.5	95.7	122.6	138.8
	(c) 14 days in water and 3 months in air before immersion.				
10	Sol. 8, NaCl, 1 per cent	74.0	156.7	115.3	122.3
11	Sol. 6, Na_2CO_3, 1 per cent	133.7	144.1	138.9	161.5
	(3) Neat Ideal in solutions of mixed salts.				
	(a) 7 days in water before immersion.				
17	Sol. 11, $CaCl_2$, $MgCl_2$, NaCl, 1.33 per cent each	73.1	81.0	77.0	109.6
16	Sol. 10, NaCl, Na_2SO_4, $MgCl_2$, $MgSO_4$, 1.25 per cent each	109.3	68.2	88.7	156.1
	(b) 3 months in water before immersion.				
14	Sol. 10, NaCl, Na_2SO_4, $MgCl_2$, $MgSO_4$, 1.25 per cent each	90.6	92.1	91.3	144.9
	(c) 48 hours in damp oven before immersion.				
33	Sol. 10, NaCl, Na_2SO_4, $MgCl_2$, $MgSO_4$, 1.25 per cent each	51.6	68.8	60.2	146.1
	(4) Neat Ideal to show effects of titration.				
37	In water. Titrated daily with H_2SO_4*	65.0	66.0	65.5	134.6
43	Sol. 14, NaCl, Na_2SO_4, 2.5 per cent each. Titrated weekly with H_2SO_4†	91.5	52.8	72.1	175.0
39	In water. Titrated daily with H_2SO_4‡	68.2	78.3	73.2	143.3
45	Sol. 4, Na_2SO_4, 5 per cent. Titrated weekly with H_2SO_4‡	78.8	55.8	67.3	147.1

*Water changed weekly.
†Solution not changed.
‡Water changed after each test for strength.

Given Periods in Salt Solutions Expressed as Per Cent of the Strength for a Similar Length of Time.

months		After being in solution: 24 months			30 months			40 months			84 months		
Tension	Average	Comp.	Tension	Average	Comp.	Tension	Average	Comp.	Tension	Average	Comp.	Tension	Average
%	%	%	%	%	%	%	%	%	%	%	%	%	%
100	100	100	100	100	100	100	100	100	100	100	100	100	100
138.8	137.1	106.5	136.5	121.5	95.8	134.4	115.1	76.2	110.1	93.1	76.8	78.1	77.8
67.3	114.9	118.3	38.7	78.5	91.9	96.1	94.0	81.7	90.2	85.9	55.7	80.1	67.9
55.8	102.6	112.0	108.1	110.0	94.2	107.0	100.6	91.6	102.9	97.2	69.1	91.6	80.3
89.9	103.9	73.6	96.1	84.9	59.4	103.5	81.4	66.0	93.1	79.5	50.2	117.8	84.0
92.1	127.1	121.3	54.9	83.1	103.2	41.3	72.2	105.8	55.6	80.7	81.8	138.9	110.3
126.3	123.9	104.2	123.4	113.8	80.8	35.8	103.3	74.7	113.2	93.1	94.9	.....	.....
93.4	112.0	57.5	39.8	48.6	40.5	96.7	68.6	51.1	67.1	59.1	25.4	121.0	73.2
126.3	122.3	107.7	113.5	110.6	73.6	112.5	93.0	.....	.....	.....	.....	.....	.....
115.9	132.5	108.0	96.2	102.1	90.8	106.3	98.5	105.2	100.2	102.6	90.5	.....	.....
118.2	121.8	92.9	101.6	97.2	89.3	107.6	98.4	124.2	105.0	114.6	62.6	249.6	156.1
108.8	123.8	119.1	127.2	123.1	93.6	131.7	112.6	96.2	116.9	106.5	94.3	87.3	90.8
186.4	104.3	96.3	100.5	98.4	77.9	94.5	86.2	80.4	87.4	83.7	65.1	91.6	78.3
97.8	129.6	.....	.....	.....	103.0	99.2	101.1	107.6	81.1	94.3	63.2	131.7	97.4
46.9	78.2	92.6	119.9	102.2	72.9	117.7	95.3	88.1	99.1	93.6	61.5	111.9	86.7
112.0	134.0	86.9	113.9	100.4	74.4	110.0	92.2	79.4	114.0	96.7	.....	47.6	.....
127.9	136.4	80.3	106.5	93.4	74.1	119.2	91.6	76.4	126.8	101.6	34.7	13.1	23.9
41.4	93.7	103.3	148.3	120.8	67.1	167.0	117.0	80.1	174.7	122.4	59.5	83.7	71.6
101.3	117.9	106.3	89.5	97.9	97.1	102.2	98.6	107.7	37.6	72.6	.....	.....	.....
81.1	123.0	118.5	117.5	118.0	99.3	106.3	102.3	101.4	144.5	122.9	78.8	147.2	113.0
66.2	104.7	101.5	112.2	111.3	110.9	121.2	116.0	107.3	118.7	113.0	97.8	84.9	91.3
125.9	136.5	103.3	107.9	105.6	84.3	127.0	105.6	97.8	109.1	103.4	.....	.....	.....

Tables IV and V.

Lab. No.	SOLUTION	IV—Compression strength of mortars; varying proportions of sand and different solutions.				V—Compression strength of mortars at ends of periods expressed in percentages of compression strength before immersion.			
		Before immersion	After being in solution			Before immersion	After being in solution		
			6mo.	12mo.	18mo.		6 mo.	12mo.	18mo.
		lbs.	lbs.	lbs.	lbs.	%	%	%	%
60½	1:1 Mortar, N. NaCl and N. Na_2SO_4	5372	8590	9167	7612	100.0	159.5	170.6	141.6
61	1:1 mortar, N. $MgCl_2$ and N. $MgSO_4$	4975	5770	6162	4982	100.0	115.9	123.8	100.1
62	1:2 mortar, N. NaCl and N. Na_2SO_4	2330	4017	3262	2487	100.0	172.4	140.0	106.7
63	1:2 mortar, N. $MgCl_2$ and N. $MgSO_4$	2027	2542	1462	585	100.0	125.4	72.1	29.0
64	1:3 mortar, N. NaCl and N. Na_2SO_4	1002	1810	415	*	100.0	180.6	41.4	*
65	1:3 mortar, N. $MgCl_2$ and N. $MgSO_4$	755	917	315	*	100.0	121.4	41.7	*
66	1:4 mortar, N. NaCl and N. Na_2SO_4	347	1345	1142	291	100.0	387.6	329.1	83.8
67	1:4 mortar, N. $MgCl_2$ and N. $MgSO_4$	697	567	123	*	100.0	81.3	17.6	*
68	1:5 mortar, N. $MgCl_2$ and N. $MgSO_4$	467	930	617	*	100.0	199.1	132.1	*
69	1:5 mortar, N. $MgCl_2$ and N. $MgSO_4$	415	265	*	.....	100.0	63.8	*	.....

*Indicates that the cement was so weakened that it could be crushed by hand.

TABLES VI, VII, VIII.

Lab. No.	SOLUTION	VI. Compression strength of neat cement in solution kept at temperature of boiling water for 8 hours daily during 18 months.				VII. Compression strength of neat cement after each period expressed in percentages of strength before immersion.				VIII. Compression strength of neat cement after each period expressed in percentages of strength of No. 70 (assumed to be 100%).			
		Before immersion	After being in solution			Before immersion	After being in solution			Before immersion	After being in solution		
			6 mo.	12 mo.	18 mo.		6 mo.	12 mo.	18 mo.		6 mo.	12 mo.	18 mo.
		lbs.	lbs.	lbs.	lbs.	%	%	%	%	%	%	%	%
70	Hot distilled water; always under water	9097	8670	8972	10922	100	96.4	98.6	120	100	100	100	100
71	Hot distilled water; allowed to get dry periodically	10800	9380	8022	8270	100	86.8	74.2	76.5	118.7	108.1	89.4	75.7
72	Hot distilled water; 3 liters of fresh water daily	9200	7242	6427	7485	100	78.7	69.8	80.1	101.1	83.5	71.5	68.5
73	Hot saturated Na_2SO_4	9382	11095	8015	6122	100	118.2	85.4	65.2	103.1	127.9	89.3	56.0
74	Hot saturated Na_2CO_3	8622	8427	8880	8012	100	97.7	103.0	92.9	94.8	97.1	98.9	73.3
75	Hot saturated NaCl	9125	11120	9227	12735	100	121.8	101.1	139.5	100.3	128.2	102.8	116.5
76	Hot saturated $MgSO_4$	9325	8335	9015	9775	100	89.3	96.6	104.8	102.6	96.1	100.4	89.4
77	Hot saturated $MgCl_2$	8325	7057	6207	*	100	84.7	74.5	*	91.5	81.3	69.2	*
78	Cold distilled water	8532	11847	10812	15145	100	138.8	126.7	177.5	93.7	136.6	120.5	138.6
79	Hot N. NaCl and Na_2SO_4	9185	10715	8827	9492	100	116.6	96.1	103.3	100.9	123.5	98.3	86.9
80	Air	11277	11772	11237	12192	100	104.3	99.6	108.1	123.4	135.7	125.1	111.6
81	Hot N. $MgCl_2$ and $MgSO_4$	10030	7862	6590	2365	100	78.3	65.7	23.5	110.2	90.6	73.4	21.6
82	Hot N. Na_2CO_3 and N. NaCl	7867	10880	8800	11460	.....	.....	.....	.....	86.4	125.4	98.0	104.9
83	Hot N. Na_2CO_3 and N. Na_2SO_4	7402	10192	9612	11640	.....	.....	.....	.....	81.3	117.5	107.1	106.5
84	Hot N. $MgSO_4$ and N. NaCl	7822	9410	5457	4797	.....	.....	.....	.....	85.9	108.5	60.8	43.9

*Completely disintegrated.

TABLE IX—*Strength of 1:1 mortars of five brands of cement and of cements receiving special treatments before being put in solutions.*

Lab. No.	SOLUTION	Before immersion		After being in solution							
				12 months		24 months		30 months		84 months	
		Comp.	Tens.	Comp.	Tens.	Comp.	Tens.	Comp.	Tens.	Comp.	Tens.
		lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
46	Ideal, in distilled water	6457	434	9987	571	8472	766	10232	756	12912	495
22	Ideal, 1.5 p. c. each: Na_2CO_3, NaCl, Na_2SO_4	8165	693	8270	844	10202	800	9265	877	11830	744
23	Ideal, 1.25 p. c. each: NaCl, Na_2SO_4, $MgSO_4$ $MgCl_2$	7118	661	6160	816	5278	571	4517	702	5747	.....
40	Iron ore, 3 p. c. each: Na_2CO_3, NaCl, Na_2SO_4	3256	426	7802	859	10425	959	10217	989	13720	865
50	Iron ore, 3 p. c. each: Na_2CO_3, NaCl, Na_2SO_4	4032	522	9172	877	9952	930	10717	936	13065	732
51	Alkali Proof, 3 p. c. each: Na_2CO_3, NaCl, Na_2SO_4	4095	552	5955	766	7935	875	7125	852	9042	725
44	Apple, 3 p. c. each: Na_2CO_3, NaCl, Na_2CO_4	4157	471	8950	812	9370	859	10137	800	12292	530
49	Atlas, 3 p. c. each: Na_2CO_3, NaCl, Na_2CO_4	4505	588	8760	861	8445	916	9480	882	12670	576
	The following 1:1 Ideal cement mortars were specially treated; solution contained 3 per cent of each: Na_2CO_3, NaCl, Na_2SO_4:										
24	Mixed with 5 per cent H_2SO_4	6752	662	7330	509	9265	862	8565	867	12195	572
28	Mixed with 1 per cent each: H_2SO_4, Na_2HPO_4	5967	656	7705	815	7777	807	8495	779	11177	775
47	Mixed with 5 per cent H_2SO_4	4282	488	9355	802	10287	870	10432	917	11296	576
48	Mixed with 2 per cent H_2SO_4	3725	532	9265	886	9185	952	9857	974	12212	595
52	Mixed with 2 per cent H_2SO_4	4502	492	9176	931	10975	986	10597	941	12475	603
53	Mixed with 2 per cent H_2SO_4	4258	551	9152	932	11320	939	10955	909	13685	610
54	Mixed with 1 per cent H_2SO_4	3476	488	9362	874	9722	967	10157	872	12085	572
35	Mixed with 5 per cent of aceticaldehyde	6313	684	6390	492	7260	612	7612	647	8865	581
34	Painted with 3 coats of Nico C*	5026	812	7052	660	8067	625	9452	730	12807	741

*After the first period the paint was off.

TABLE X—*Strength of neat "alkali proof" cements (in water 7 days before immersion).*

Lab. No.	SOLUTION	Before immersion		After being in solution							
				15 months		20 months		25 months		84 months	
		Comp.	Tens.	Comp.	Tens.	Comp.	Tens.	Comp.	Tens.	Comp.	Tens.
		lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
85	1 per cent Na_2SO_4	3868	466	9830	780	9677	942	9705	735	.....	115
86	10 per cent Na_2SO_4	2613	431	10163	886	8667	860	8457	888	.....	139
87	5 per cent $MgSO_4$	5385	657	6990	907	8450	489	8005	942	9562	392
88	5 per cent Na_2SO_4	3310	387	11000	929	11097	365	10545	931	13887	205
89	5 per cent $MgSO_4$	3735	352	3033	996	10192	1021	8350	931	8673	210
90	5 per cent Na_2CO_3	3315	383	9247	630	8705	696	9847	659	10978	207
91	5 per cent Na_2SO_4 (30 days in water)	6011	768	6410	889			6545	709	11997	265

TABLE XI—*Strength of 1:3 Ideal mortars with different protecting coatings.*

Lab. No.	Solution: 3 per cent each, NaCl, Na_2SO_4 Na_2CO_3. One month in water before the waterproofers were applied.	Before immersion		After being in solution						Strength after 24 months=100. Change during last period	
				12 months		24 months		84 months			
		Comp.	Tens.	Comp.	Tens.	Comp.	Tens.	Comp.	Tens.	Comp.	Tens.
		lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	%	%
55	Mixed with Conn paste	6362	430	7207	825	7265	836	10872	452	+49.6	—45.9
56	2 coatings of Toch's Liquid Konkerit	5647	882	8892	697	9432	676	10878	571	+15.3	—15.5
57	2 coatings of Toch's Cement Floor Paint	4085	675	6910	884	8985	849	10252	462	+14.1	—45.5
58	2 coatings of Toch's No. 44 R. I. W.	6130	799	8775	820	7857	776	8975	485	+14.2	—37.5
59	2 coatings of Toch's No. 232 R. I. W.	5140	830	5810	800	6540	790	10045	560	+53.5	—29.1

After the first period of 12 months the coatings were greatly swollen up and could be easily rubbed off, except the one on No. 59, which lasted for 24 months, after which time it also was useless as a surface protector. Consequently, during the last long period the cements were without any surface protection. It is noteworthy that in all cases the compression strength increased, while the tension strength decreased during the last period.

Table III. Showing the chemical composition of [illegible] after [illegible] months immersion in various solutions.

Lab. No.	Solutions	Water of constitution	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O and K_2O	SO_3	Cl	CO_2	Total	Organic matter by difference
		%	%	%	%	%	%	%	%	%	%	%	%
30	(1) Distilled water	21 2	18.86	14.13	6.33	2.67	2.96	1.44	1.21	*Trace	0.94	101.64	
	(2) In solutions of single salts												
	(a) 7 days in water before immersion.												
1	$SnCl_4$ 5 per cent	18 87	15 24	42 26	3 45	1 75	3 46		4 75	5 16	0 97	99 28	1 32
2	[illegible]	17 76	7 11	39 31	1 45		33	1 43	31	5 25	1 8	97 53	
3	[illegible]	18 16	11 32	40 04	1 73		35	2	2 21	6 35	*Trace	98 52	
4	[illegible]	18	12	39	1		35	2	2	6	0 33	98	
5	[illegible]	20 83	14 17	32 31	1 02		33	2 46	1 16	0 95	0 41	98 77	
	(b) 8 [illegible]	17 5	13 21	40 16	5 02	2 22	1 63	2 66	11 38	0 14	0 65	100 21	0 14
6	$Sn(SO_4)_2$ 5 per cent	17 4	12 52	42 09	4 39	2 07	2 01	2 59	6 73	2 57	1 25	100 45	0 48
7	$SnCl_4$ 5 per cent	18	10	42	3	1	1	3	5	0 93	0 44	100	0 84
8	[illegible]	18	13	42	4	1	1	3	5	3	1	100	0
9	[illegible]	18	13	43	5	1	1	3	5	0	0	100	0
10	[illegible]	18	13	43	5	1	1	3	5	0	0	100	0
	(c) 14 days in water and 3 months in air before immersion	18 09	11 93	39 05	6 75	3 19	0 24	1 62	9 50	0 98	0 84	101 47	0 98
15	$SnCl_4$ 1 per cent	18 09	15 84	50 08	7 75	3 15	0 92	1 26	4 68	1 92	0 25	95 51	1 92
16	[illegible]	18	15	41	7	3	0	2	5	0	0	99	0
	(3) In mixtures of various salts, 1 gram in each solution. 7 days in water before immersion.												
14	1.25 per cent each of $SnCl_4$, $Sn(SO_4)_2$, $MgCl_2$ and $MgSO_4$	18 13	21 29	36 99	7 62	2 58	3 22	4 16	7 67	5 96	0 59	101 44	1 44
16	Same as No. 14	18 74	19 61	38 89	8 99	3 44	4 67	2 42	3 45	2 39	*	101 13	1 79
17	1.25 per cent each of $SnCl_4$, $MgCl_2$ and $SnCl_4$	20 09	19 77	45 16	3 [illegible]	1 13	3 17	1 95	6 36	1 88	*	102 95	1 82

*Very little; not determined.

DISCUSSION OF THE DATA.

The chief reacting substance in the cement is lime, in the form of calcium hydroxide. It may be formed either from the hydration of the calcium oxide present in the clinker, or may be formed during the setting of cement. With the sulfate salts of sodium and magnesium it forms calcium sulfate, $CaSO_4.2H_2O$, and sodium hydroxide with the former and magnesium hydroxide with the latter. The ratio of the molecular volume of calcium sulfate formed in the reaction to the molecular volume of calcium hydroxide is as 1.98:1. The sodium hydroxide formed in reaction with sodium sulfate remains in solution. In the case of magnesium sulfate, the ratio of the molecular volume of calcium sulphate plus the magnesium hydroxide formed in the reaction to the molecular volume of calcium hydroxide originally in the cement is as 2.78:1. In Bulletin 81 of Montana Experiment Station, the disintegration of cement is ascribed as being due to this formation of compounds with larger molecular volumes, causing expansion and consequent cracking. Another theory, similar to the above, is held by several experimenters. According to this theory, tricalcium-aluminium sulfate is formed, and this then causes the expansion and disintegration of cement. In Technologic Paper No. 12 of the Bureau of Standards, by Messrs. Bates, Phillips, and Wig, data is produced to disprove this theory.

Turning to the data given in tables 1 and 2, based on an 84 month period of action, we find that the changes in compression strength and changes in tension strength do not always go parallel; one may increase while the other may decrease, and vice versa. The 5% solution of sodium sulfate affected the compression strength more than any other solution of one salt only, cement thus treated having only 25.4% of the compression strength of cement in distilled water for the same length of time. The next lowest compression strength was shown by cement in following solutions: Magnesium sulfate (55.7%), sodium bicarbonate (62.6%), sodium chloride (76.8%), and sodium carbonate (90.5%). The solution of sodium sulfate was used in 3 different concentrations: 1%, 5% and 10%, and the compression strength of cement kept in these solutions was 69.1%,

50.2% and 81.8% respectively at the end of 84 months. It also appears that cement which has been in ordinary or distilled water for a longer period was affected more strongly, thus cement 14 days in water before immersion in a 5% solution of sodium sulfate only had a compression strength equal to 25.4%.

It is a noticeable fact that the compression strength after 84 months is rather high in most cases, but that the tension strength is low, even for cement which was kept in distilled water. On the average, it is only 50 per cent of the tension strength which the cement had before immersion. This difference between compression and tension strength becomes more noticeable when considering the effects of solutions which contained more than one salt. In the case of solution No. 10, which contained the sulfates and chlorides of sodium and magnesium, when the tension strength of cement, which was in water 14 days and 3 months before immersion in solution, was only 120 and 34 lbs. respectively. The tension strength of cement which was only 48 hours in a damp oven before immersion in solution No. 10 at the end of 84 months still was 211 lbs., thus showing again that younger cement is less affected.

The compression and tension strength of cement in different sets recorded in the table was not the same for all sets before immersion in solutions. Regardless of what the strength was before immersion, in all cases the maximum was reached sometime during the experiment, and this maximum is very nearly the same. In every case recorded, even in the case of cement which was in water 3 months previous to immersion in a solution, the compression as well as the tension strength always increased after the immersion in a solution until the maximum was reached. If the formation of molecules which have larger volumes than the original compounds of set cement is the cause of the disintegration of cement, then this would be more pronounced soon after immersion, for then the formation of $CaSO_4.2H_2O$ would be faster than it would be later. Consequently, the decrease of strength should be most noticeable during the reaction. The facts do not show this to be true. The progress of the formation of hydrated calcium sulfate from lime and sodium sulfate can be followed by determining the amount of sodium hydroxide formed in the re-

action. This was done by titrating the solution to neutral with sulfuric acid. The procedure was carried on until no more sodium hydroxide was formed, which was after 24 months. At this time the cement should be the weakest. Figure 20 represents graphically the change of compression strength and the amount of acid required to neutralize the sodium hydroxide formed, the neutralizing being done every day. Instead of the expected decrease of strength during this reaction, there was an increase.

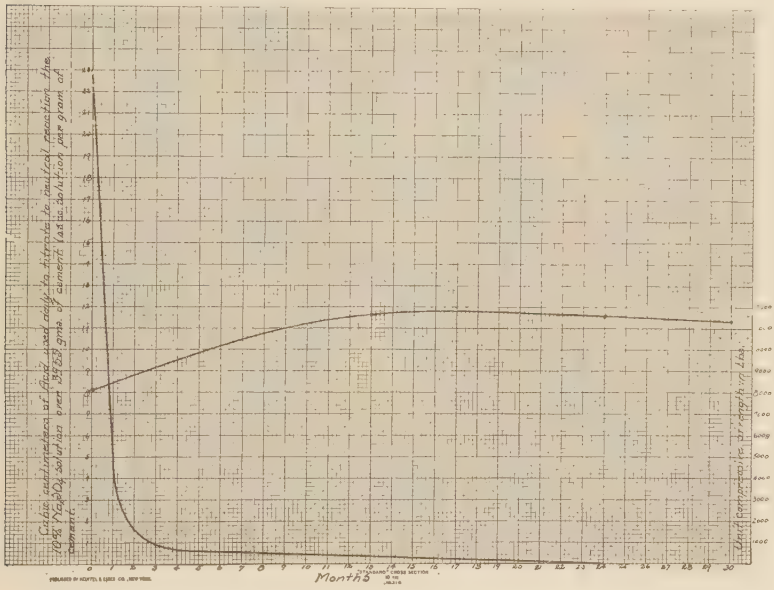

Fig. 20.

Besides, the cement in magnesium sulfate solution should have a lower strength than cement in sodium sulfate solution. The results show that this is not the case. This does not mean that the formation of reaction products, which have larger molecular volumes than the reagents in the cement, does not contribute towards disintegration. But it is not the chief cause or the only cause of disintegration.

In tables 6, 7 and 8 are given the strength values of cement kept in solution at the temperature of boiling water. The results

after a period of 18 months are characteristic. The set which was completely disintegrated is the one which was in a solution of magnesium chloride, while the cement in a solution of magnesium sulfate had an average compression strength of 9775 lbs., and cement in a solution of sodium sulfate, 6122 lbs. Noteworthy is the fact that cement kept in solution containing both magnesium chloride and sulfate still had a strength of 2365 lbs., and cement in a solution containing magnesium sulfate and sodium chloride, 4797 lbs. Evidently the solution of sodium chloride did not produce any bad effect, since the strength of cement in it was 12735 lbs., while the strength in hot distilled water was only 10922 lbs. These results suggest the following questions: Why did magnesium chloride have the strongest disintegrating effect? Why did the solution of magnesium chloride containing also magnesium sulfate produce a slower decrease in strength than the solution containing magnesium chloride alone? Why was the strength of cement kept in the solution of magnesium sulfate containing also sodium chloride 50 per cent less than the strength of cement in the solution of magnesium sulfate alone, although the solution of sodium chloride did not produce any bad effects?

The answer to the first question is the fact that magnesium chloride in solution undergoes hydrolysis, the result of which is the formation of hydrochloric acid. It is then this hydrochloric acid which attacks the cement. The hydrolysis of magnesium chloride in solution goes on to a lesser extent when magnesium sulfate is also present in solution. For this reason the disintegrating effect of a solution containing both salts is less severe for equal periods.

When magnesium sulfate and sodium chloride are dissolved together in water, the solution contains 4 salts instead of two. This may be expressed by the following equation: $MgSO_4 + 2NaCl \leftrightarrows MgCl_2 + Na_2SO_4$. The magnesium chloride thus produced hydrolizes and the result of this reaction is the formation of hydrochloric acid: $MgCl_2 + H_2O \leftrightarrows Mg(OH)_2 + HCl$. As the dydrochloric acid reacts with the components of the cement, it is being removed, so to speak, and the result of this is that the above reactions gradually progress toward the right.

Results analogous to those obtained in hot solutions were also obtained from experiments on mortars with various proportions of sand. Again, the magnesium chloride solution had the most rapid disintegrating effect and other solutions in the same order as above. But the results in this table show also that as the proportion of sand in the mortar increases the disintegration is hastened. The data in these tables are in agreement with conclusions from figures 16, 17 and 18. Although for numbers 60, 61 and 62 the strength after 18 months in solution is higher than the strength which the mortars had before immersion, nevertheless there is a decided decrease of strength after the maximum had been reached.

The data recorded in table 9 were meant to give a comparison of the resistance to action of alkali by 1:1 mortars prepared with cements of different brands. The comparison of sets 22 and 23 is interesting. Apparently the presence of sodium carbonate in the solution counteracted the disintegrating effect. No. 22 in a solution containing sodium carbonate, sulfate and chloride after 84 months had higher compression strength (11830 lbs.) than the cement No. 60 in solution of sodium chloride and sulfate had after 18 months (7612 lbs). The same is also true for tensile strength. These results are graphically represented in figures 21 and 22 for compression and tension strength respectively.

The cements, of brands tried, do not show very much difference in compression strength. The "Alkali-proof" cement had the lowest compression, below normal, while the others did not show any decrease. The tensile strength of all of them, although still higher than the tensile strength of cement in distilled water, show distinctly a decrease after the maximum had been reached. It is noteworthy that the cements which were made up with solutions of sulfuric acid of various concentrations and also kept in the above solution (containing sodium carbonate, sulfate and chloride) had normal compression strength, but the tensile strength also had decreased during the last period. The cement which was mixed with a solution containing one per cent of sulfuric acid and di-sodium-hydrogen phosphate, at the end of 84 months in the above solution had normal compression strength and the

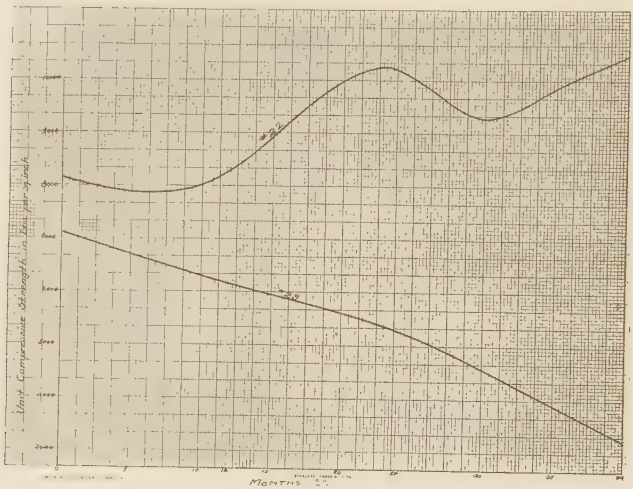

Fig. 21.

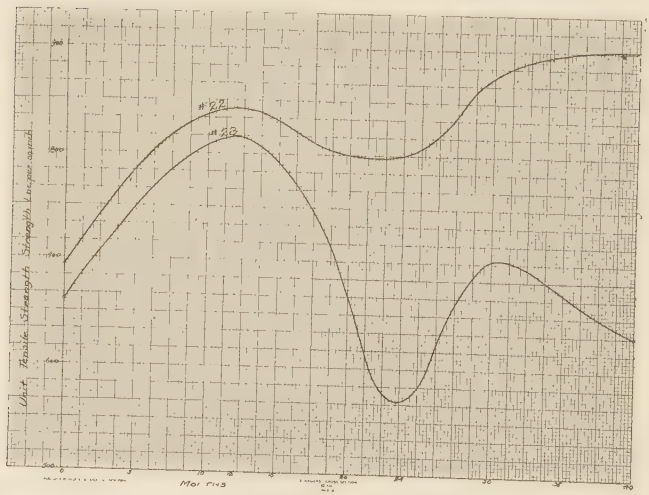

Fig. 22.

tensile strength (775 lbs.), did not decrease during the last 54 months. The results obtained from sets 24, 28, 47, 48, 52, 53, 54 show that it is safe and also an advantage to use weak sulfuric acid (1-5%) for mixing up cement. On the other hand, when

a solution was used for mixing which contained an organic substance, a distinctly inferior cement was obtained. The results with the "Alkali-proof" cement are represented in table 10. It is evident that its tensile strength suffered greatly after the maximum had been reached, regardless of what the solution was. Here, too, a comparison between the results in this table and No. 51 in table 9 distinctly show that the solution which contained sodium carbonate was less harmful.

For testing out the value as surface protectors against the action of alkali of different commercial paints recommended as waterproofers, 1:3 mortar was covered with them. The mortar of each set received 2 coatings of some one paint. After 24 months in a solution of sodium carbonate-sulfate-chloride the paints were off. That the paints after that did not offer resistance to penetration of solutions is shown by the marked decrease of tensile strength during the last period of 60 months. Although the Nico C paint was off after 12 months, some of the ingredients of the paint must have had a beneficial effect as protectors, since in this even the tensile strength did not decrease during the last period of 50 months.

In actual practice cement frequently is only periodically exposed to the action of alkali. This change of conditions from wet and dry itself has a deteriorating effect on the cement. In set No. 71 the cement was periodically wet and dry and the result was that its compression strength was 25% less than that of cement which was under water constantly. The solvent effect of large volumes of water also comes in play, as seen from No. 72. This cement was treated with 3 liters of fresh distilled water every day during a period of 18 months and the result is that its compression strength at the end of this period was 31.5% less than the compression strength of cement which was under the same conditions, except that the water never was changed. In nature, the disintegration of cement is the result of all the enumerated causes combined, and besides it is accelerated by freezing and thawing.

The entire procedure might be described as follows: Cement of any age, when put in solutions of salts of magnesium, or sodium, as a rule, shows an increase of strength. This continues

until a maximum is reached. During this period the reaction between the salts and the calcium hydroxide takes place and if any bad effects are produced from these reactions, they are not marked by a decrease in the strength of the cement. The cause of this may be that the increase in strength during this period is greater than the decrease. The calcium sulfate or calcium carbonate, as the case may be, increases the density of cement and makes it less pervious to the solutions. Besides, the calcium sulfate has a binding value, which may reach 200-300 lbs. This was tried out on halves of a broken briquet; they were cemented together and it took that much force to full them apart. When the compounds of the cement other than the calcium hydroxide are attacked, then the decrease of strength begins to show. As the table of analyses shows, the extent of chemical changes is comparatively small. What the changes may be can to some extent be judged from the analysis of the crystals shown in figure 7. The effect of magnesium chloride is more marked than the effect of the other salts because the hydrochloric acid formed due to hydrolysis reacts with the fundamental compounds of cement. In the case of chlorides, the calcium chloride formed is removed from the cement, while in the case of sulfates, the calcium sulfate is deposited. The experiments with equivalent solutions of hydrochloric and sulfuric acids show that the former is more harmful. After 6 months the strength of cement in hydrochloric acid decreased 22%, in sulphuric acid only 16%. The difference may be due to the fact that the calcium sulfate formed makes the cement less permeable. That the mortars are more rapidly destroyed than the neat cement is to be expected. For the same weight, they contain less of the reacting material, but expose as much surface to the action of solutions as neat cement. Consequently, a greater proportion of their cement content has been reached in shorter time. The effects from the reactions are augmented by the dissolving action which increases the porosity of cement, by the friction of particles carried in suspension, by the wearing away of the weakened surface layers, thus exposing deeper layers of cement, and, finally, by the formation of cracks due to uneven expansion and contraction, through which the solution also penetrates deeper into the cement. Any process which

will make the cement less porous and less permeable to the solutions will also increase its resistance to the action of alkali. In this connection, attention may be called to the behavior of cement which was not mixed with water but with solutions containing ions forming insoluble calcium salts. Results with oxalic acid (5%) used for mixing the cement and which, after setting, was put in a hot solution of N. sodium sulfate and N. sodium chloride were as follows: Compression strength before immersion, 8502; after 6 months in solution, 10742; after 12 months, 10280, and after 18 months, 13685 lbs. Cement mixed with a solution of magnesium flouride had a compression strength before immersion 6087 lbs; after 6 months in the above sodium-chloride-sulfate solution, 9499 lbs., and after 18 months, 15580. Since these substances and also the sodium phosphate and sulfuric acid are not very expensive, their solutions could be used in cement practice.

The results with a hot saturated calcium sulfate solution are not recorded in the tables. The compression strength of cement varied as follows: Before immersion, 7240; after 6 months, 9452; 12 months, 8745; 18 months, 11710.

Evidently the calcium sulfate solution did not have any bad effect upon the strength of cement.

SUMMARY

Cement put in solutions of salts which constitute the "alkali" sets as well as in water.

In solutions of sodium sulfate, or magnesium sulfate $CaSO_4$. $2H_2O$ is formed and NaOH and $Mg(OH)_2$ respectively.

A solution of magnesium chloride had the greatest disintegrating effect, due to the action of hydrochloric acid produced by the hydrolysis of this salt.

A sodium sulfate solution was more harmful than a solution of magnesium sulfate, other conditions being equal.

The presence of sodium chloride in solutions of sulfates of sodium and magnesium increased their harmful effect on cement.

A five per cent solution of sodium sulfate had a stronger effect than either the 1 per cent or 10 per cent solutions.

The presence of sodium carbonate in solutions of the other salts retards the disintegrating effects.

Compression strength and tensile strength are not affected in the same degree; tensile strength decreases more rapidly in all solutions, even when compression strength increases.

Solutions of calcium sulfate had no bad effects

Water-proofing paints offer protection only for short periods

The "iron-ore" cement resisted the action of sodium carbonate-sulfate-chloride solution; the other cements tried had somewhat lower tensile strength.

The mixing of cement in weak solutions of sulfuric acid, di-sodium phosphate, magnesium flouride and oxalic acid is of advantage and increases the alkali resisting qualities.